Chemical Physics 32 (1978) 11–15

DYNAMIC CHARGE DISTRIBUTION OF PYRAZINE: HARTREE–FOCK–SLATER CALCULATION AND COMPARISON WITH X-RAY DIFFRACTION RESULTS*

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Received 10 February 1978

The dynamic charge distribution of pyrazine (1,4-diazabenzene) has been calculated using a Hartree–Fock–Slater type wavefunction. The calculations were done in direct space employing a Taylor-series expansion. The calculated charge distribution shows approximate agreement with the results of an accurate X-ray diffraction experiment. A discussion of several factors affecting the agreement between experimental and theoretical results is given.

1. Introduction

The calculation of the dynamic (difference) charge distribution from the static one, is a process of averaging over vibrational motion.

In molecular crystals we may distinguish internal ("molecular") and external ("lattice") vibrational modes. Averaging of the charge distribution over internal modes requires that the static charge distribution is available at several geometries of the molecule. In general this is not the case. Furthermore, in a model calculation on ethyne [1] the effect of the internal vibrations appeared to be negligible. Hence we restrict ourselves to the external vibrations.

The external vibrations are the (rigid body) translations and librations, described by the translation tensor **T** and libration tensor **L**. The coupling between translation and libration is described by the screw-tensor **S**. If the molecule occupies a centro-symmetric site in the crystal the **S**-tensor vanishes identically [2]. This is the case for pyrazine [3], for which accurate X-ray data are available.

* This research has been carried out under the auspices of the Foundation for Fundamental Research on Matter by Electron and X-rays (FOMRE) and with aid from the Netherlands Organization for Advancement of Pure Research (ZWO).
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2. The dynamic charge distribution

In the case of rigid body translations and librations only, the dynamic charge distribution $\rho_{dyn}(r)$ is obtained from the static charge distribution $\rho_{sta}(r)$ by

$$\rho_{dyn}(r) = \int\int \rho_{sta}(r - u_{tra} - u_{lib}(r, \omega)) \times P_{tra}(u_{tra}) P_{lib}(\omega) \, du_{tra} \, d\omega . \quad (1)$$

$P_{tra}(u_{tra})$ is the probability density function (pdf) describing the probability that the point r is displaced over a distance u_{tra}, due to the translations. The vector u_{tra} is independent of r; its components are denoted by u_x, u_y and u_z. $P_{lib}(\omega)$ is the pdf describing the probability that a libration $|\omega|$ about a unit vector $\omega/|\omega|$ takes place, resulting in a (librational) displacement $u_{lib}(r, \omega)$ for the point r. In the harmonic approximation the pdf's for translations and librations are given by

$$P_{tra}(u_{tra}) = (2\pi)^{-3/2} (\det \mathbf{T}^{-1})^{1/2} \times \exp(-\tfrac{1}{2} r^t \cdot \mathbf{T}^{-1} \cdot r) , \quad (2)$$

and

$$P_{lib}(\omega) = (2\pi)^{-3/2} (\det \mathbf{L}^{-1})^{1/2} \times \exp(-\tfrac{1}{2} \omega^t \cdot \mathbf{L}^{-1} \cdot \omega) , \quad (3)$$

respectively.

If the mean square displacements due to librations are small, $u_{\mathrm{lib}}(r, \omega)$ may be approximated by [4]

$$u_{\mathrm{lib}}(r, \omega) = \mathbf{R} \cdot \omega = \begin{pmatrix} 0 & z & -y \\ -z & 0 & x \\ y & -x & 0 \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \\ \gamma \end{pmatrix}, \quad (4)$$

where x, y and z are the components of r and α, β and γ the components of ω in the principal axes frame of the **L**-tensor. This approximation assumes linear displacements for the librational motion.

Several approaches are possible for the calculation of $\rho_{\mathrm{dyn}}(r)$. If the basis functions, from which $\rho_{\mathrm{sta}}(r)$ was calculated, are of the gaussian type, a direct analytic evaluation [1,5] or a calculation via Fourier-space [6,7] of $\rho_{\mathrm{dyn}}(r)$ is possible. In the latter procedure the effect of the Fourier-series termination can be included.

A different procedure is followed here. In the neighbourhood of any point, r, ρ_{sta} may be described by a three dimensional Taylor-series

$$\rho_{\mathrm{sta}}(x + \Delta x, y + \Delta y, z + \Delta z) = \sum_j c_j(x, y, z) \Delta x^{k_j} \Delta y^{l_j} \Delta z^{m_j}, \quad (5)$$

where c_j is the expansion coefficient and k_j, l_j and m_j the exponents. Substitution of (5) in (1) yields a sum of moments of the different pdf's. In the case of small mean square librations each term in the sum can be factorized into a product of moments of the individual pdf's. The latter can be evaluated analytically.

If we also assume the principal axes of the **T**-tensor to coincide with those of the **L**-tensor the final result becomes

$$\begin{aligned} \rho_{\mathrm{dyn}}(r) = \sum_j c_j & \int (-u_x)^{k_j} P_x(u_x)\,\mathrm{d}u_x \\ & \times \int (-u_y)^{l_j} P_y(u_y)\,\mathrm{d}u_y \int (-u_z)^{m_j} P_z(u_z)\,\mathrm{d}u_z \\ & \times \int (z\alpha)^{l_j} (-y\alpha)^{m_j} P_\alpha(\alpha)\,\mathrm{d}\alpha \\ & \times \int (-z\beta)^{k_j} (x\beta)^{m_j} P_\beta(\beta)\,\mathrm{d}\beta \\ & \times \int (y\gamma)^{k_j} (-y\gamma)^{m_j} P_\gamma(\gamma)\,\mathrm{d}\gamma, \end{aligned} \quad (6)$$

where

$$P_{\mathrm{tra}}(u_{\mathrm{tra}}) = P_x(u_x) P_y(u_y) P_z(u_z), \quad (7)$$

and

$$P_{\mathrm{lib}}(\omega) = P_\alpha(\alpha) P_\beta(\beta) P_\gamma(\gamma), \quad (8)$$

have been used.

3. Results and discussion for pyrazine

Previously it was shown that the Hartree–Fock–Slater (HFS) method [8] yields charge distributions of accuracy comparable with the Hartree–Fock method [12,13].

Hence for the calculation of $\rho_{\mathrm{sta}}(r)$ of pyrazine a HFS wavefunction was used. It was also shown that one should use a double zeta basis plus d functions on each atom for a reliable description of the charge distribution. In this work the exponents of s and p functions were chosen accordingly to Clementi [9] while the exponents of the d functions are due to McLean and Yoshimine [10]. The geometry as found from X-ray work was used [3]. Atomic densities calculated from a HFS wavefunction employing the same basis set, were subtracted in order to obtain the difference charge distribution.

The coefficients c_j in expression (5) were determined by a least-squares fit to the values of ρ_{sta}, evaluated at a three dimensional grid about the point r under consideration. The sum $k_j + l_j + m_j$ was $\leqslant 4$. A 125 point grid with a step size of 0.1 Å in each direction was used. Trial calculations with a somewhat larger as well as a somewhat smaller step size yielded very similar results.

The additional simplification of taking the principal axes of the **T**-tensor to be the same as those of the **L**-tensor is allowed for pyrazine; the principal values of this constrained **T**-tensor do not differ significantly from the original ones [3] whereas the fit to the individual atomic temperature factors was only slightly worse.

Along several lines in the pyrazine molecule $\rho_{\mathrm{dyn}}(r)$ was calculated. The results are shown in fig. 1. Comparison of the ρ_{dyn}-curves with the experimental curves shows only approximate agreement. Differences in the bond peaks amount to 2 or 3 standard deviations, in the lone pair peaks somewhat more. The average standard deviation in $\rho^{\mathrm{obs}}_{s_{\max}}$, $\sigma(\rho)$ was estimated as 0.035 $e/\mathrm{Å}^3$ [3]. However, the goodness of fit S was 1.68. Hence a better estimate of $\sigma(\rho)$ is 0.060 $e/\mathrm{Å}^3$. Besides

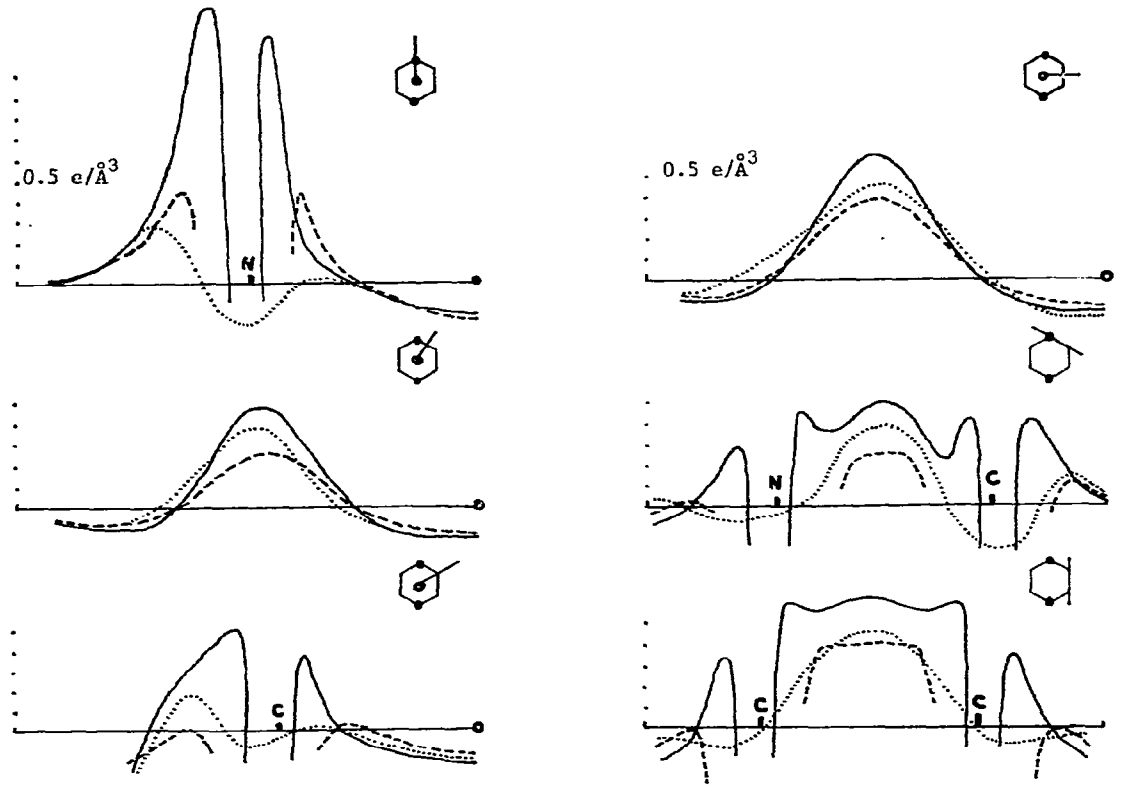

Fig. 1. Comparison of $\rho_{sta}(r)$ (—), $\rho_{dyn}(r)$ (---) and $\rho^{obs}_{s_{max}}(r)$ (...) along several lines in the molecule as indicated in the inserts. In these inserts the dots denote the nitrogen atoms. The small circles indicate the centre of the molecule.

$\sigma(\rho)$ increases near the symmetry line along the nitrogen lone pair lobe.

An analogous calculation with only a T-tensor fitted to the individual temperature factors (table 1) yielded very similar curves. This effect, that the dynamic density is largely independent on the exact form of the thermal smearing function has been observed before [11].

The fit of (5) to $\rho_{sta}(r)$ is bad near the nuclei, due to the high curvature of $\rho_{sta}(r)$. Hence, the resulting $\rho_{dyn}(r)$ is unreliable in that region and not shown in fig. 1. This presents no serious problem in comparing the experimental and theoretical charge distribution as the accuracy of the experimental charge density is relatively low in the core region.

Theoretical peak heights (table 2) are systematically lower then the observed ones, except for the lone pair lobe of the nitrogen atom. A fair agreement is found between the observed and theoretical widths as half-height of the peaks. A similar result was found by Stevens et al. [22].

A discussion of several factors affecting the agree-

Table 1
Principal components of a T- and L-tensor fitted to the individual temperature factors [a]

T ($Å^{-2}$)	0.0269	0.0364	0.0287
L (deg^2)	4.4	15.6	10.8

Principle components of a T-tensor only fitted to the individual temperature factors

T ($Å^{-2}$)	0.0335	0.0422	0.0348

[a] Taken from ref. [3].

Table 2
Peak heights and widths at half-height

Peak	Height (e/Å^3)		Width (Å)	
	exp.	theor.	exp.	theor.
N lone pair	0.27	0.43	0.47	0.29
CN bond ⊥	0.38	0.27	0.63	0.72
CC bond ⊥	0.46	0.38	0.90	0.80
CN bond ∥	–	–	0.63	0.51
CC bond ∥	–	–	0.71	0.74
CH bond ∥	0.15	0.02	–	–

ment between observed and calculated curves (fig. 1) is given below.

(*a*) The accuracy of the HFS wavefunction. Some evidence has been found that HFS wavefunctions are not as good as Hartree–Fock (HF) wavefunctions, for molecules containing second-row atoms [11]. Apart from results on CO [12] and N_2 [13] no comparison of charge densities evaluated by the HFS and HF method has been made for molecules containing only first-row atoms. Since these two investigations report a good agreement between the HFS and HF charge densities, we do not expect the accuracy of the HFS method to be insufficient in the present case.

(*b*) The influence of the crystal field. For the nitrate ion the influence of the crystal field has been estimated as small [14]. The crystal field in that case is probably stronger, since it is – at least partially – "ionic", while in pyrazine only "van der Waals" interaction takes place. On the other hand the polarizability of pyrazine ($\approx 9 \times 10^{-24}$ cm^{-3} †) is higher than that of the nitrate ion ($\approx 4 \times 10^{-24}$ cm^{-3} †). The relative importance of both aspects is hard to estimate.

(*c*) The size of the basis set. For CO [12] the difference between the charge distribution as calculated from a HF-limit wavefunction and a DZ + d wavefunction was small. Hence we do not expect the quality of the basis set to be insufficient.

(*d*) The inaccuracy of the experimental data. The structures of pyrazine in the solid phase and the gas-phase agree well [16]. Hence only errors in the temperature factor remain. A separate investigation using neutron diffraction should be carried out in order to check the temperature factors. Their precise values are not of critical importance for the calculation of $\rho_{dyn}(r)$, since this quantity is to a large extent independent of the exact form of the thermal smearing function. This is not true for the experimental difference charge distribution, which is critically dependent on accurate values of the temperature factors (compare ref. [3]).

(*e*) The influence of internal vibrations. As mentioned in the introduction, it is difficult to deal with internal vibrations. The separation of the internal and external vibrational modes is roughly 300 cm^{-1} [17, 18]. The molecule is thus fairly rigid. (Compare also the order of magnitude of the amplitudes as found from a gas-phase electron diffraction experiment [16]).

(*f*) The limitations of the Taylor expansion procedure. The results of this procedure have been compared with the results of direct numerical integration of (1) for a number of points. No significant differences were observed.

(*g*) The effect of series termination. In the treatment outlined before the effect of series termination can be approximately taken into account. The experimental charge distribution $\rho^{obs}_{s_{max}}(r)$ as obtained from a finite Fourier summation is related to ρ_∞ (the charge distribution as obtained from the corresponding infinite Fourier summation) by [19]

$$\rho^{obs}_{s_{max}}(r) = \int \rho_\infty(r - r')S(r')\,dr' ,$$

with

$$S(r) = \tfrac{4}{3}\pi(s_{max}/2\pi)^3\, 3(\sin r - r\cos r)/r^3 ,$$

and

$$s_{max} = 4\pi(\sin\theta_{max})/\lambda .$$

This has to be compared with

$$\rho^{calc}_{s_{max}}(r) = \int \rho_{dyn}(r - r')S(r')\,dr . \qquad (11)$$

Using once more a Taylor expansion for $\rho_{sta}(r)$ (see eq. (7)), integrals of the kind

$$\int x^{(n)} \sin ax \exp(-bx^2)\,dx \qquad (12)$$

arise, for which no analytic solution exists for $n \leqslant -1$ [20]. However, if we replace the function $S(r)$ by a Gauss-function [21] of the same volume and peak height

$$S(r) \rightarrow (a/2\pi)^{3/2} \exp(-\tfrac{1}{2}a\mathbf{r}^t \cdot \mathbf{r}) , \qquad (13)$$

† Estimated from atomic contributions [15].

with $a = (4\pi/3)^{2/3}(2\pi)^{-1}s_{max}^2$ we recover the sum of moments formula (8), but with the exponents of the pdf for translation [eq. (2)] changed as follows.

$$-\tfrac{1}{2}r^t \cdot \mathbf{T}^{-1} \cdot r \rightarrow -\tfrac{1}{2}r^t \cdot (\mathbf{T}^{-1} + a) \cdot r . \qquad (14)$$

A cut-off of $(\sin\theta)/\lambda = 0.85$ Å^{-1} is equivalent to an extra artificial temperature factor of 0.021 Å^{-2}. The corresponding smearing of $\rho_{dyn}(r)$ will result in an additional lowering of the peak heights. Since most of the theoretical curves are beneath the experimental ones, the agreement becomes worse. However, the ripples of the function $S(r)$ may lead to either an enhancement or a reduction of the charge density values.

The effect of thermal motion and series termination can be accounted for exactly if the Fourier transform of $\rho_{sta}(r)$ is available. This procedure seems indeed the best approach [11]. The procedure as outlined in this paper, however, can be used to estimate quickly the decrease in peak heights in $\rho_{sta}(r)$ due to thermal motion and series termination.

Acknowledgement

Many thanks are due to dr. E.J. Baerends (Free University of Amsterdam, The Netherlands) for calculating the HFS wave function and to dr. S. Harkema (Twente University of Technology, Enschede, The Netherlands) for helpful discussions.

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